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(54) **Paste, display member, and process for production of display member**

(57) A display member, particularly a plasma display member, can be produced by a process comprising applying a paste which comprises a urethane compound

and inorganic particles onto a substrate and then firing the paste, so providing a display member having a post-firing pattern without any defect.

EP 1 158 019 A2

Description

[0001] The present invention relates to a paste and a process for the production of a display member using the paste. The paste and the process of the present invention can be used for the production of various types of displays, including a plasma display, a plasma address liquid crystal display and a field emission display, and, for example, for pattern processing in circuit materials.

[0002] In the fields of displays and circuit materials, increasingly small and high-definition products have been recently developed and pattern processing techniques adaptable to such development have been demanded. In particular, for the production of a barrier rib for a plasma display, methods have been demanded which enable the pattern processing of inorganic materials, such as glass, with high accuracy and high aspect ratio.

[0003] Heretofore, for the pattern processing of inorganic materials, methods have been proposed in which pattern formation is performed using a photosensitive paste by photolithography technique, as disclosed in JP-A-09-310030 and US-A-6197480.

[0004] However, when using such methods a problem arises in that a firing shrinking force caused by crosslinking of an organic component is generated at the time of removing the organic component by firing, leading to the occurrence of defects such as peeling and line breaking of the pattern. We have made intensive and extensive studies for the purpose of providing a paste which causes no defect such as peeling and line breaking during firing.

[0005] Thus, according to a first aspect, the present invention provides a paste comprising a urethane compound and (preferably fine) inorganic particles.

[0006] According to a second aspect, the present invention provides a paste comprising (preferably fine) inorganic particles and an organic component, which paste, when heated to 500°C and 1,000°C, has respective weights at these temperatures which satisfy the following equation:

$$(\text{weight at } 500^{\circ}\text{C}) / (\text{weight at } 1,000^{\circ}\text{C}) \leq 1.05.$$

[0007] According to a third aspect, the present invention provides a paste comprising (preferably fine) inorganic particles and an organic component, which paste, when applied onto a silicon wafer into a thin film and then heated to 500°C, has a calculated maximum value of the average film stress, based on the quantity of warping of the silicon wafer caused by shrinkage of the thin film, from 0.1 to 20 MPa.

[0008] According to a fourth aspect, the present invention provides the use of a paste according to any previous aspects of the invention, for producing a display, particularly a plasma display.

[0009] According to a fifth aspect, the present invention provides a process for producing a display member, which process comprises applying a paste comprising a urethane compound and inorganic fine particles onto a substrate and then firing the paste.

[0010] Preferred embodiments of the invention will now be described.

[0011] A paste according to the present invention comprises an organic component and (preferably fine) inorganic particles. The "organic component" refers to the total of any component or components of organic material in the paste, other than the inorganic particles. The paste of the present invention can be used for the formation of a pattern consisting substantially of inorganic material(s) in such a manner that the pattern is formed with the paste by any of various methods and the pattern is then fired to remove the organic component, thereby forming the pattern.

[0012] A pattern consisting substantially of the inorganic material(s) produced using the paste of the present invention is preferably used in a display, particularly as a barrier rib of the rear plate of a plasma display panel for a plasma display.

[0013] A paste in accordance with the first aspect of the invention contains, and respective pastes in accordance with the second and third aspects of the invention preferably contain, as the organic component, or as at least one of the organic components a urethane compound.

[0014] In addition to the urethane compound and the inorganic particles, such a paste may contain a binder polymer, a dispersing agent, a plasticizer, a thickener, an organic solvent, a precipitation preventive agent, an antioxidant and so on, as required.

[0015] The urethane compound which may be used in a paste embodying the present invention preferably has a molecular weight ranging from 15,000 to 50,000. As used herein, the term "molecular weight" refers to a weight average molecular weight. When the molecular weight of the urethane compound is 15,000 or higher, the flexibility of the urethane can be maintained and defects such as peeling of patterned portions and line breaking during firing can be decreased to a larger extent. When the molecular weight of the urethane compound is 50,000 or lower, the viscosity of the urethane can be decreased so that the urethane becomes easy to handle.

[0016] The urethane compound which may be used in a paste embodying the present invention includes, for example, a compound represented by formula (1):



wherein R¹ and R² are independently selected from a substituent having an ethylenic unsaturated group, a hydrogen atom, a C₁-C₂₀ alkyl group, a C₁-C₂₀ aryl (typically C₆-C₁₅ aryl) group, a C₁-C₂₀ aralkyl (typically C₇-C₁₆ aralkyl) group and a C₁-C₂₀ hydroxyaralkyl (typically hydroxy C₇-C₁₆ aralkyl) group; R³ is an alkylene oxide group or an alkylene oxide (typically ethoxy and/or propoxy) oligomer; R⁴ is an organic group having a urethane bond; and n is an integer of from 1 to 10.

[0017] The urethane compound preferably contains an ethylene oxide unit. More preferably, R³ in formula (1) is an oligomer containing an ethylene oxide unit and a propylene oxide unit, and the content of the ethylene oxide unit in the oligomer is in the range of from 8 to 70 wt%. When the content of the ethylene oxide unit is 70 wt% or smaller, the flexibility of the urethane can be improved and the stress caused at the time of barrier rib formation can be reduced. As a result, occurrence of defects such as line breaking of the barrier rib can be prevented effectively. In addition, the property of thermal decomposition can be improved, reducing the firing residues in the firing process after the barrier rib formation. When the content of the ethylene oxide unit is 8 wt% or higher, the compatibility of the urethane compound with other organic components can be improved. The compatibility among the organic components can be determined based on the haze of a coating film formed by applying the organic components. A smaller haze value indicates a better compatibility in which the organic components are more sufficiently dissolved in each other. It is preferred that a film on which the organic components are applied at a thickness of 30 μm show a haze value of not larger than 5.0%. In the present invention, the haze is determined by "the test method for optical properties of a plastic" in accordance with JIS K7105. In this method, the haze (H; in %) can be determined by measuring a diffusion transmittance (Td) and a total transmittance (Tt) using an integrating sphere ray transmittance measuring apparatus and then calculating the ratio between them [i.e., H = (Td/Tt)x100]. More preferably, the haze is not larger than 0.8%, still more preferably not larger than 0.5%.

[0018] R⁴, the organic group having a urethane bond, is preferably produced by condensation between a component having an isocyanate group and a component having a hydroxyl group. The component having the isocyanate group is preferably a polyisocyanate, especially a diisocyanate compound and such compounds which may be used in the condensation reaction include an aliphatic diisocyanate compound (e.g., 1,4-diisocyanatobutane and 1,6-diisocyanatohexane); an aromatic diisocyanate compound (e.g., 1,4-phenylene diisocyanate and tolylene diisocyanate); and an alicyclic diisocyanate compound (e.g., 1,4-cyclohexylene diisocyanate and isophorone diisocyanate). Among these, a more preferred diisocyanate compound is an alicyclic diisocyanate compound, particularly isophorone diisocyanate. The component having the hydroxyl group is preferably a polyhydroxy, especially a dihydroxy compound.

[0019] Specific examples of the urethane compound include, but are not limited to, UA-2235PE (M.W.: 18,000, EO content: 20%), UA-3238PE (M.W.: 19,000, EO content: 10%), UA-3348PE (M.W.: 22,000, EO content: 15%), UA-2349PE (M.W.: 27,000, EO content: 7%), UA-5348PE (M.W.: 39,000, EO content: 23%), all of these products being made by SHINAKAMURA KAGAKU KOGYO KK. These compound may be used in combination.

[0020] The content of the urethane compound is preferably 0.1 to 20 wt% based on the weight of the paste. A content of not lower than 0.1 wt% enables the provision of a satisfactory peeling-preventing effect. If the content is higher than 20 wt%, then the dispersibility of the organic component and the inorganic fine particles may be reduced and, as a result, defects may occur.

[0021] A paste embodying the present invention may additionally contain any one or more of, for example, a reactive monomer, a reactive oligomer, a reactive polymer, a photopolymerization initiator, a photo acid generating agent, a photo base generating agent, a sensitizer, a sensitizing auxiliary, an ultraviolet ray absorber, an organic dye, an acid and a base, so that the paste can be used as a photosensitive paste. As used herein, the term "reactive" used in "a reactive monomer", "a reactive oligomer" and "a reactive polymer" means that, when the paste is irradiated with an active light, the reactive monomer, the reactive oligomer or the reactive polymer undergoes a reaction, such as photocrosslinking, photopolymerization, photo-depolymerization or photo-denaturation, thereby to change the chemical structure of the paste. In this case, a display member may be produced using the paste by photolithography technique.

[0022] Each of the reactive monomer, reactive oligomer and reactive polymer preferably has an ethylenic unsaturated bond therein. More preferably, prior to irradiation with an active light, the ethylenic unsaturated bond is present in the paste in a concentration of from 0.2 to 1.0 mol per kg of the paste. When the concentration of the ethylenic unsaturated bond in the paste is 0.2 mol or higher, the sensitivity of the paste can be maintained and a good pattern-forming property can be achieved. When the concentration of the ethylenic unsaturated bond is 1.0 mol or lower, the density of crosslinking at the time of pattern formation can be maintained in a proper range and binder removability becomes good. In addition, the polymerization shrinkage caused by application of light or heat can be reduced and, as a result, peeling of the patterned portions or line breaking can be largely prevented.

[0023] A paste embodying the present invention preferably further contains an amine compound having an ethylenic

unsaturated group therein as the reactive monomer. It is particularly preferable for the paste to contain at least one of the amine compounds represented by formula (3) and (4), since the sensitivity of the paste to light may be improved:



and



wherein R^5 is a substituent having an ethylenic unsaturated group; R^6 , R^7 and R^8 are independently selected from a substituent having an ethylenic unsaturated group, a hydrogen atom, a C_1 - C_{20} alkyl group, a C_1 - C_{20} aryl (typically C_6 - C_{15} aryl) group, a C_1 - C_{20} aralkyl (typically C_7 - C_{16} aralkyl) group and a C_1 - C_{20} hydroxyalkyl group; and M is a bivalent linkage group.

[0024] The substituent R^5 containing an ethylenic unsaturated group in the amine compound is preferably represented by any one of formulae (5), (6) and (7):



wherein R^9 is a hydrogen atom or a methyl group; A is COO, CONH or a substituted or unsubstituted phenylene group; L is selected from a C_3 - C_{20} cyclic or C_1 - C_{20} acyclic alkylene group, a C_6 - C_{20} arylene group and a C_7 - C_{20} aralkylene group, which may be unsubstituted or substituted with, for example, at least one of a C_1 - C_6 alkyl group, a halogen atom, a hydroxyl group and an aryl (e.g. C_6 - C_{20} aryl, especially optionally substituted phenyl) group; and each of a and b independently is 0 or 1.

[0025] More preferably, R^9 is $CH_2=C(CH_3)COOCH_2CH(OH)CH_2-$.

[0026] The amine compound which may be used is preferably a tertiary amine compound. A particularly preferable example of the compound is represented by formula (8):



wherein R^{10} is a hydrogen atom or a methyl group; R' is an alkyl (e.g. C_1 - C_{10} alkyl), aryl (e.g. C_6 - C_{20} aryl, especially optionally substituted phenyl), aralkyl (e.g. C_7 - C_{20} aralkyl, especially optionally substituted benzyl) or hydroxyalkyl (especially hydroxy- C_1 - C_{10} alkyl) group; Z is -O- R'' - or -NHR''- wherein R'' is an alkylene (e.g. C_1 - C_{10} alkylene), arylene (e.g. C_6 - C_{20} arylene), aralkylene (e.g. C_7 - C_{20} aralkylene) or hydroxyalkylene (e.g. hydroxy- C_1 - C_{10} alkylene) group; and m is 0, 1 or 2.

[0027] The most preferable amine compound which may be used in a paste embodying the present invention is bis (2-hydroxy-3-methacryloyloxypropyl) isopropylamine.

[0028] The amine compound having an ethylenic unsaturated bond may be prepared by reacting, for example, glycidyl acrylate, glycidyl methacrylate, acryloyl chloride, methacryloyl chloride, acrylic anhydride or methacrylic anhydride each having an ethylenic unsaturated bond therein with an amino compound. A plurality of compounds each having an ethylenic unsaturated bond may be used in combination. The amine compound having an ethylenic unsaturated bond may be any of those compounds as mentioned above (or even others), and may be used in combination.

[0029] In a paste embodying the present invention, a reactive monomer having an ethylenic unsaturated bond other than the above-mentioned amine compounds may be used, as required. The reactive monomer may be a monomer having therein at least one photopolymerizable acrylate, methacrylate or allyl group. Specific examples of the monomer include an acrylate or methacrylate of an alcohol (e.g., ethanol, propanol, hexanol, octanol, cyclohexanol, glycerol,

trimethylolpropane and pentaerythritol); a reaction product of a carboxylic acid (e.g., acetic acid, propionic acid, benzoic acid, acrylic acid, methacrylic acid, succinic acid, maleic acid, phthalic acid, tartaric acid and citric acid) with glycidyl acrylate, glycidyl methacrylate, acrylglycidyl or tetraglycidyl meta-xylylenediamine; an amide derivative (e.g., acrylamide, methacrylamide, N-methylolacrylamide, methylene-bis(acrylamide)); and a reaction product of an epoxy compound with acrylic or methacrylic acid. In a polyfunctional monomer, the unsaturated group may be a combination among acrylic, methacrylic, vinyl and allyl groups. These compounds may be used singly or in combination.

[0030] As the reactive oligomer, it is preferable to use a urethane compound having an ethylenic unsaturated group therein. The ethylenic unsaturated group in the urethane compound can react with an ethylenic unsaturated group in a reactive monomer or a reactive polymer, so that the urethane compound is incorporated in the crosslinking product. As a result, the polymerization shrinkage can be reduced more effectively.

[0031] A paste embodying the present invention may contain a copolymer having a carboxyl group therein.

[0032] For the preparation of the copolymer having a carboxyl group, for example, a monomer containing a carboxyl group (e.g., acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinylacetic acid and the anhydrides of these compounds) or a monomer (e.g., a methacrylate, an acrylate, styrene, acrylonitrile, vinyl acetate and 2-hydroxyacrylate) may be selected and then subjected to copolymerization using an initiator such as azobisisobutyronitrile.

[0033] Preferable examples of the copolymer having a carboxyl group include a copolymer of an acrylate or methacrylate and acrylic acid or methacrylic acid as copolymerization components, because such a copolymer has a low thermal decomposition temperature during firing. Particularly preferable is styrene/methyl methacrylate/methacrylic acid copolymer.

[0034] The acid value of the copolymer having a carboxyl group is preferably in the range of from 50 to 150 mg KOH/g. When the acid value is 150 mg KOH/g or lower, the allowable range of development can be extended. When the acid value is 50 mg KOH/g or higher, the solubility of the unexposed regions in terms of the developer is not decreased. As a result, peeling of the exposed regions can be prevented and high-definition patterns can be obtained without the necessity of increasing the concentration of the developing solution.

[0035] It is also preferable for the copolymer having a carboxyl group also to have an ethylenic unsaturated group in its side chain. Such an ethylenic unsaturated group includes an acrylic group, a methacrylic group, a vinyl group and an allyl group.

[0036] The addition of such a side chain to the copolymer can be achieved, for example, by the addition reaction between a mercapto group, an amino group, a hydroxyl group or a carboxyl group in the copolymer and an ethylenic unsaturated compound having a glycidyl or isocyanate group, acrylyl chloride, methacrylyl chloride or allyl chloride.

[0037] Examples of the ethylenic unsaturated compound having a glycidyl group include glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, glycidyl ethyl acrylate, crotonyl glycidyl ether, crotonic acid glycidyl ether and isocrotonic acid glycidyl ether. Examples of the ethylenic unsaturated compound having an isocyanate group include acryloylisocyanate, methacryloylisocyanate, acryloyl ethylisocyanate and methacryloyl ethylisocyanate. The ethylenic unsaturated compound having a glycidyl or isocyanate group, acrylyl chloride, methacrylyl chloride or allyl chloride is preferably added in an amount of 0.05 to 1 mole equivalent for each equivalent of the mercapto group, amino group, hydroxyl group or carboxyl group in the polymer.

[0038] To achieve a proper exposure level, it is preferred to add the copolymer having a carboxyl group in an amount of 10 to 90 wt% based on the weight of the organic components except solvents.

[0039] When a binder component is needed, polyvinyl alcohol, polyvinyl butyral, a methacrylate polymer, an acrylate polymer, an acrylate-methacrylate copolymer or butyl methacrylate resin may be used as a polymer.

[0040] The photopolymerization initiator usable in the present invention may be selected from those initiators which can generate a radical species. Specific examples of the photopolymerization initiator include diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl) ketone, 1-hydroxycyclohexyl-phenyl ketone, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, 2-methyl-[4-(methylthio)phenyl]-2-morpholynopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholynophenyl)-butanone-1, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzophenone, methyl o-benzoylbenzoate, 4-phenylbenzophenone, 4,4-dichlorobenzophenone, hydroxybenzophenone, 4-benzoyl-4'-methyl-diphenyl sulfide, alkylated benzophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone, 4-benzoyl-N,N'-dimethyl-N-[2-(1-oxo-2-propenyloxy)ethyl]benzenemethanaminium bromide, (4-benzoylbenzyl)trimethylammonium chloride, 2-hydroxy-3-(4-benzoylphenoxy)-N,N,N-trimethyl-1-propanaminium chloride monohydrate, 2-isopropylthioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2,4-dichlorothioxanthone, 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-N,N,N-trimethyl-1-propanaminium chloride, 2,4,6-trimethylbenzoylphenylphosphine oxide, 2,2'-bis(o-chlorophenyl)-4,5,4',5'-tetraphenyl-1,2-bimidazole, 10-butyl-2-chloroacridone, 2-ethylanthraquinone, benzyl, 9,10-phenanthrenequinone, camphorquinone, methylphenylglyoxyester, η^5 -cyclopentadienyl- η^6 -cumenyl-iron(1+)-hexafluorophosphate(1-), a diphenylsulfide derivative, bis (η^5 -2,4-cyclopentadien-1-yl)-bis (2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium, 4,4-bis(dimethylamino)benzo-

phenone, 4,4-bis(diethylamino)benzophenone, thioxanthone, 2-methylthioxanthone, 2-chlorothioxanthone, 4-benzoyl-4-methylphenyl ketone, dibenzyl ketone, fluorenone, 2,3-diethoxyacetophenone, 2,2-dimethoxy-2-phenyl-2-phenylacetophenone, 2-hydroxy-2-methylpropiophenone, p-t-butylidichloroacetophenone, benzyl methoxyethyl acetal, anthraquinone, 2-t-butylanthraquinone, 2-aminoanthraquinone, β -chloroanthraquinone, anthrone, benzanthrone, dibenzosuberone, methyleneanthrone, 4-azidobenzalacetophenone, 2,6-bis(p-azidobenzylidene)cyclohexane, 2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone, 2-phenyl-1,2-butadione-2-(o-methoxycarbonyl)oxime, 1,3-diphenylpropanetrione-2-(o-ethoxycarbonyl)oxime, naphthalenesulfonyl chloride, quinolinesulfonyl chloride, N-phenylthioacridone, 4,4-azobisisobutyronitrile, benzthiazole disulfide, triphenylphosphine, carbon tetrabromide, tribromophenylsulfone, benzoyl peroxide, and a combination of a photoreducing dye (e.g., Eosine or Methylene Blue) and a reducing agent (e.g., ascorbic acid or triethanolamine).

[0041] In a paste embodying the present invention, one or more of these compounds may be used. The photopolymerization initiator is preferably added in an amount of 0.05 to 10 wt%, more preferably 0.1 to 10 wt%, based on the total of the organic component. When the photopolymerization initiator is added within this range, a good photosensitivity can be achieved while maintaining a sufficient remaining ratio of the exposed regions.

[0042] A sensitizer may be used together with the photopolymerization initiator to improve the sensitivity and expand the wavelength range which is effective for the reaction. Specific examples of the sensitizer include 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, 2-isopropylthioxanthone, 2,3-bis(4-diethylaminobenzal)cyclopentanone, 2,6-bis(4-diethylaminobenzal)cyclohexanone, 2,6-bis(4-diethylaminobenzal)-4-methylcyclohexanone, Michler's ketone, 4,4-bis(diethylamino)benzophenone, 4,4-bis(dimethylamino)chalcone, 4,4-bis(diethylamino)chalcone, p-dimethylaminocinnamylideneindanone, p-dimethylaminobenzylideneindanone, 2-(p-dimethylaminophenylvinylene)isonaphthothiazole, 1,3-bis(4-diethylaminophenylvinylene)isonaphthothiazole, 1,3-bis(4-diethylaminobenzal)acetone, 1,3-carbonylbis(4-diethylaminobenzal)acetone, 3,3-carbonylbis(7-diethylaminocoumarin), triethanolamine, methyldiethanolamine, triisopropanolamine, N-phenyl-N-ethylethanolamine, N-phenylethanolamine, N-tolyldiethanolamine, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, isoamyl dimethylaminobenzoate, isoamyl diethylaminobenzoate, (2-dimethylamino)ethyl benzoate, (n-butoxy)ethyl 4-dimethylaminobenzoate, 2-ethylhexyl 4-dimethylaminobenzoate, 3-phenyl-5-benzoylthiotetrazole and 1-phenyl-5-ethoxycarbonylthiotetrazole.

[0043] In a paste embodying the present invention, one or more of these initiators may be used. Some of the sensitizers can also be used as photopolymerization initiators. The sensitizer is preferably added to the paste of the present invention in an amount of 0.05 to 10 wt%, more preferably 0.1 to 10 wt%, based on the weight of the organic component. When the amount of the sensitizer is in this range, a good photosensitivity can be achieved while maintaining a satisfactory remaining ratio of the exposed regions.

[0044] In a paste embodying the present invention, it is preferred to add an antioxidant to the paste. An antioxidant is a component having functions of radical polymerization inhibition, triplet scavenging and hydroperoxide decomposition.

[0045] When the paste is used for the production of a barrier rib for a plasma display member and numerous fine glass particles are present in the paste, occurrence of light scattering within the paste caused by exposure light cannot be avoided. As a result, spreading of the shape of a barrier rib pattern and filling of spaces between patterns (i.e., formation of film remnants) which are considered to be caused by such light scattering are liable to occur. It is desirable that the wall face of a barrier rib pattern have a rectangular shape which rises perpendicularly. Ideally, the paste coating film which has been exposed with light is dissolved in a developing solution at a certain exposure level or lower, but is not dissolved at an exposure level not lower than the certain exposure level. In other words, the coating film can be dissolved in a developing solution even at a low exposure level due to the light scattering and, therefore, spreading of the shape of a barrier rib pattern and filling of spaces between patterns hardly occur at a higher exposure level, advantageously expanding the range of the exposure level at which the development can be achieved.

[0046] An antioxidant may be added to the paste. In this case, the antioxidant can trap radicals and return the energy state of the excited photopolymerization initiator or sensitizer back to the ground state. As a result, any unnecessary photo-reaction caused by scattered light can be prevented, and a photo-reaction can occur rapidly at an exposure level which cannot be prevented by the antioxidant, leading to the production of a high contrast between dissolution and non-dissolution of the paste in the developing solution.

[0047] Specific examples of the antioxidant include p-benzoquinone, naphthoquinone, p-xyloquinone, p-toluquinone, 2,6-dichloroquinone, 2,5-diacetoxy-p-benzoquinone, 2,5-dicaproxy-p-benzoquinone, hydroquinone, p-t-butyl catechol, 2,5-dibutylhydroquinone, mono-t-butylhydroquinone, 2,5-di-t-amylhydroquinone, di-t-butyl-p-cresol, hydroquinone monomethyl ether, α -naphthol, hydrazine hydrochloride, trimethylbenzylammonium chloride, trimethylbenzylammonium oxalate, phenyl- β -naphthylamine, parabenzylaminophenol, di- β -naphthylparaphenylenediamine, dinitrobenzene, trinitrobenzene, picric acid, quinonedioxime, cyclohexanoneoxime, pyrogallol, tannic acid, triethylamine hydrochloride, dimethylaniline hydrochloride, cupferron, (2,2-thiobis(4-t-octylphenolate)-2-ethylhexylaminonickel-(II), 4,4'-thiobis-(3-methyl-6-t-butylphenol), 2,2'-methylenebis-(4-methyl-6-t-butylphenol), 2,2'-thiobis-(4-methyl-6-t-butylphenol), triethyleneglycol-bis[3-(t-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis[(3,5-di-t-butyl-4-hydroxypheno-

nyl)propionate] and 1,2,3-trihydroxybenzene. In a paste embodying the present invention, one or more of these compounds can be used.

[0048] The amount of the antioxidant to be added is preferably 0.1 to 30 wt%, more preferably 0.5 to 20 wt%, based on the weight of the paste. When the amount of the antioxidant is in this range, the photo-sensitivity of the paste can be maintained and a satisfactory polymerization degree can be maintained. As a result, a high contrast between dissolution and non-dissolution of the paste in the developing solution can be achieved while maintaining the desired pattern shape.

[0049] The paste may contain an ultraviolet ray absorber to absorb scattered light within the paste caused by irradiation with exposure light, resulting in weakening of the scattered light. The ultraviolet ray absorber may be, for example, a benzophenone compound, a cyanoacrylate compound, a salicylate compound, a benzotriazole compound, an indole compound or a fine particulate inorganic metal oxide. Among these, a benzophenone compound, a cyanoacrylate compound, a benzotriazole compound or an indole compound is particularly effective. Specific examples of these compounds include 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxy-5-sulfobenzophenone, 2-hydroxy-4-methoxy-2'-carboxybenzophenone, 2-hydroxy-4-methoxy-5-sulfobenzophenone trihydrate, 2-hydroxy-4-n-octoxybenzophenone, 2-hydroxy-4-octadecyloxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 4-dodecyloxy-2-hydroxybenzophenone, 2-hydroxy-4-(2-hydroxy-3-methacryloxy)propoxybenzophenone, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-5'-di-t-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-4'-n-octoxyphenyl)benzotriazole, 2-ethylhexyl-2-cyano-3,3-diphenylacrylate, 2-ethyl-2-cyano-3,3-diphenylacrylate and commercially available indole-type absorbers, "BONASORB" UA-3901, "BONASORB" UA-3902 and SOM-2-0008 (all of these products are produced and sold by Orient Chemical Industries, Ltd.). Each of these ultraviolet ray absorbers may be used in a reactive form in which a methacrylic group or the like is introduced to its backbone. In a paste embodying the present invention, one or more of these compounds can be used.

[0050] The amount of the ultraviolet ray absorber to be added is preferably 0.001 to 10 wt%, more preferably 0.005 to 5 wt%, based on the weight of the paste. When the amount of the ultraviolet ray absorber is in this range, the transmission threshold wavelength and the wavelength inclination width can be maintained in the desired ranges, and a satisfactory effect of absorbing scattered light can be achieved while maintaining satisfactory transmittance and sensitivity of the paste.

[0051] In a paste embodying the present invention, an organic dye may be added to the paste as a marker for the light exposure and development. When an organic dye is added to color the paste, the property of visual identification becomes good so that the regions where the paste remains and the regions where the paste is removed can be easily distinguished from each other at the time of development. The organic dye is preferably one which does not remain in the insulation film after firing. Specific examples of the organic dye include an anthraquinone dye, an indigoid dye, a phthalocyanine dye, a carbonium dye, a quinoneimine dye, a methine dye, a quinoline dye, a nitro dye, a nitroso dye, a benzoquinone dye, a naphthoquinone dye, a phthalimide dye and a perinone dye. A dye which can absorb light having a wavelength near the h-line and i-line, such as a carbonium dye (e.g., Basic Blue), is particularly preferable, since the effectiveness of the present invention can be achieved more advantageously. The amount of the organic dye to be added is preferably 0.001 to 1 wt%.

[0052] To control the viscosity of the paste at the time of application onto a substrate depending on the application method employed, an organic solvent may be used. The organic solvent includes, for example, methylcellosolve, ethylcellosolve, butylcellosolve, methyl ethyl ketone, dioxane, acetone, cyclohexanone, cyclopentanone, isobutyl alcohol, isopropyl alcohol, tetrahydrofuran, dimethylsulfoxide, γ -butyrolactone, bromobenzene, chlorobenzene, dibromobenzene, dichlorobenzene, bromobenzoate and chlorobenzoate. The organic solvent may be used as a mixture of two or more of these solvents.

[0053] A paste embodying the present invention preferably contains the inorganic particles in an amount of 40 to 80 wt% based on the weight of the paste. If too much of the organic component is present, the amount of materials to be removed during the firing process is increased. As a result, the time required for the firing is prolonged and, therefore, it becomes difficult to convert the coating film into inorganic film completely. Moreover, since the firing shrinkage becomes large, the thickness of the film to be applied needs to be increased for the formation of a barrier rib with a desired size. Accordingly, too much organic component is disadvantageous from the viewpoint of pattern-forming properties. It is also disadvantageous from the viewpoint of maintaining the shape of the barrier rib. When the content of the organic component in the paste is too small, on the other hand, the inorganic particles cannot be mixed or dispersed in the paste sufficiently. Moreover, problems such as reduction in application property of the paste may occur due to the increased viscosity of the paste, affecting the stability of the paste. The dispersibility of the organic component and the inorganic particles is also reduced, leading to the occurrence of defects during the firing.

[0054] The inorganic particles are preferably fine particles which may have a mean particle size up to 5 μm but, especially where the inorganic fine particles comprise a so-called low "low melting" powder (as later described), such

a powder may contain individual particles of a size up to a maximum of 35 μm .

[0055] The inorganic particles preferably comprise a so-called "low melting" glass powder preferably having a softening point under load up to 600°C and preferably having a glass transition temperature up to 550°C. More preferably, the inorganic (preferably fine) particles comprise 60 to 97 wt% of the low melting glass powder and 3 to 40 wt% of a filler having a mean particle size of 1 to 4 μm . The filler is used together with the low melting glass to control the firing shrinkage and maintain the strength of the formed barrier rib. If the content of the filler in the inorganic particles is less than 3 wt%, then the effect of addition of the filler may not be produced. If the content of the filler is more than 40 wt%, then the strength of the barrier rib may be reduced. The inorganic particles may optionally further contain not more than 30 wt% of fine oxide particles having a mean particle size of from 0.003 to 0.02 μm .

[0056] Each of the low melting glass powder and the filler preferably has a refraction index of from 1.45 to 1.65. In a paste embodying the invention, the inorganic particles may be dispersed in an organic solvent in which the organic component is dissolved. Therefore, in the coating film of the paste, the inorganic particles are present in the organic component layer in a considerably high concentration. To form a pattern on the coating film by photolithography method, the components in the paste preferably have refractive indexes close to each other. The average refractive index of the organic component used in the paste generally lies in the range from 1.4 to 1.7. Therefore, it is preferred to select inorganic particles having a refractive index as close to this range as possible. In a glass component comprising various oxides, the properties can be controlled by varying the formula of the glass component. In a paste embodying the present invention, low melting glass powder having controlled thermal properties, refraction index, etc. can be used. The low melting glass powder preferably has a refractive index of from 1.45 to 1.65, a glass transition temperature of from 400 to 550°C and a softening point under load of from 450 to 600°C. When the softening point under load is 450°C or higher, deformation of the barrier rib can be prevented in any process which is performed after the display member production and the display production. When the softening point under load is 600°C or lower, the glass powder can be melted during firing and a barrier rib having a high strength can be obtained.

[0057] The low melting glass powder preferably has a mean particle size of from 1 to 4 μm and the maximum particle size of 35 μm or smaller. This is because good filling property and dispersibility in the paste can be provided to the glass powder, application of the paste in a uniform thickness can be achieved and a good pattern-forming property can be maintained. The glass powder having such a particle size distribution is good in filling property and dispersibility in the paste. In the case where a low melting glass powder is used, since most of the powder is integrated during the firing process, a powder having considerably large particle sizes is acceptable. When the glass powder has a mean particle size in this range, the glass powder has satisfactory filling property and dispersibility, and a paste with good application property and pattern-forming property can be obtained.

[0058] The filler which may be used in a paste embodying the present invention is preferably at least one selected from a so-called "high melting" glass and cordierite having a controlled refraction index. The high melting glass powder preferably has a glass transition temperature of up to 1200°C, more preferably 500 to 1200°C and preferably has a softening point under load of up to 120°C, more preferably 550 to 1200°C.

[0059] A paste embodying the present invention may be used as a conductive paste by using fine metal particles as inorganic fine particles. When a conductive paste is used, a high-definition circuit pattern having less defects can be produced. The conductive paste can be used for the formation of an electrode for a plasma display, for example.

[0060] Preferred examples of the fine metal particles include conductive fine particles of a noble metal such as Au, Ni, Ag, Pd and Pt. These fine metal particles may be used singly or in combination. The fine metal particles may contain Cr or Rh to improve the properties of the paste at high temperatures.

[0061] When the paste is used as a photosensitive conductive paste, it is preferred that the fine metal particles in the paste have a mean particle size of from 0.5 to 5 μm . If the particle size is less than 0.5 μm , then ultraviolet ray used for the exposure may not smoothly pass through the film applied and it may become difficult to form a very fine pattern having a line width of 60 μm or less of a good conductor. If the particle size is more than 5 μm , then the surface of the circuit pattern after the application may become rough and, as a result, the accuracy of the pattern may be reduced, causing noise. The fine metal particles preferably have a specific surface of from 0.1 to 3 m^2/g . If the specific surface is less than 0.1 m^2/g , then the accuracy of the circuit pattern may be reduced. If the specific surface is more than 3 m^2/g , then the surface areas of the fine particles may become too large and, as a result, ultraviolet ray may be scattered, causing the reduction in accuracy of the pattern.

[0062] The shape of the individual fine metal particles may be of a flake-type (e.g., plate-type, cone-type and rod-type) or generally sphere-type. However, spherical particles are preferred because aggregation of the particles can be prevented and scattering of ultraviolet ray during the exposure can be reduced.

[0063] When a paste embodying the present invention is heated to 500°C and 1,000°C at a rate of 10°C/min, it is preferred that the weights of the paste at these temperature as determined using a thermogravimetric analyzer satisfy the following equation:

$$(\text{weight at } 500^{\circ}\text{C}) / (\text{weight at } 1,000^{\circ}\text{C}) \leq 1.05.$$

[0064] A smaller ratio of the weight at 500°C to the weight at 1,000°C indicates that the binder removability of the organic component is better. When the ratio is 1.05 or lower, the organic component remaining in the barrier rib is decreased and the reliability of the resulting display can be improved. The weight ratio can be reduced by the addition of a urethane compound to the paste. In particular, the addition of a urethane compound having an ethylene oxide content falling within the above-mentioned range is preferable, since the weight ratio is reduced to a greater extent. When the paste contains a compound having an ethylenic unsaturated group, the weight ratio can be controlled by controlling the concentration of the ethylenic unsaturated group.

[0065] When a paste embodying the present invention is applied on a silicon wafer into a thin film having a thickness of 3 to 10 μm and then heated to 30 to 500°C over 1 hour, it is preferred that the maximum value of the average film stress, based on the quantity of warping of the silicon wafer caused by shrinkage of the thin film, calculated in accordance with the following equation, be in the range of from 0.1 to 20 MPa, more preferably from 0.1 to 10 MPa:

$$\text{average film stress } \sigma \text{ (Pa)} = Eh^2/(1-\nu)6Rt$$

wherein $E/(1-\nu)$ is a biaxial elastic modulus of a substrate and is 1.805×10^{11} Pa for a silicon wafer; h is a thickness (m) of the substrate; R is a radius of curvature (m) of the substrate; and t is a thickness of a thin film.

[0066] When the maximum value of the average film stress is in the range of from 0.1 to 20 MPa, the shrinkage during the firing can be prevented and defects caused by firing (e.g., peeling and line breaking) can be reduced. When the maximum value of the average film stress is in the range of from 0.1 to 10 MPa, defects caused by firing can be reduced to a greater extent. The average film stress can be controlled by the addition of a urethane compound to the paste. When the paste contains a compound having an ethylenic unsaturated group, the average film stress can be controlled by controlling the concentration of the ethylenic unsaturated group.

[0067] The paste can be prepared by blending various components, such as a binder polymer, a dispersing agent, a levelling agent, a plasticizer, a thickener, an organic solvent, a precipitation preventing agent, an antioxidant, a reactive monomer, a reactive oligomer, an reactive polymer, a photopolymerization initiator, a photo acid generating agent, a photo base generating agent, a sensitizer, a sensitizing auxiliary, an ultraviolet ray absorber, an organic dye, an acid, a base and an organic solvent, in a desired composition, and then mixing and dispersing these components homogeneously using a triple roller or a kneader.

[0068] The viscosity of the paste may be properly controlled by varying the blending ratio of the inorganic fine particles, the thickener, the organic solvent, the plasticizer or the precipitation preventing agent in the paste, and is preferably in the range of from 2,000 to 200,000 cps (centipoises). For example, in the case where a spin coating method is employed for the application of the paste onto a substrate, it is preferable to adjust the viscosity to 2,000 to 5,000 cps. In the case where a screen printing method is employed for the application of the paste onto a substrate and a thin film having a thickness of 10 to 20 μm is to be formed in one application step, it is preferable to adjust the viscosity to 50,000 to 200,000 cps. In the case where a blade coater method or die coater method is employed, it is preferable to adjust the viscosity to 10,000 to 50,000 cps.

[0069] A paste embodying the present invention prepared as mentioned above may be applied onto a substrate, a pattern formed using any one of various methods and then the formed pattern fired, thereby to produce a display member. A paste embodying the present invention is particularly suitable for the production of a plasma display member having barrier ribs on a substrate. A preferred method for the pattern formation to be employed in the present invention is, for example, screen printing method, sandblasting method or photolithography method. Among these, photolithography method is particularly preferred since a highly precise processing can be achieved.

[0070] A process embodiment for the production of a display member using the paste by a photolithography method is now described as follows.

[0071] The paste is applied over the entire surface or a part of a substrate to form a coating film. The application of the paste may be performed using, e.g., screen printing method, bar coater method, roll coater method, die coater method or blade coater method. The thickness of the coating film can be controlled by selecting the time of respective applications, a screen of desired mesh size and the viscosity of the paste.

[0072] When the paste is applied onto the substrate, the surface of the substrate may be treated to achieve a close contact between the substrate and the coating film. Agents which may be used for such surface treatment include a silane coupling agent such as vinyl trichlorosilane, vinyl trimethoxy silane, vinyl triethoxy silane, tris(2-methoxyethoxy) vinyl silane, γ-glycidoxypentyl trimethoxy silane, γ-(methacryloxypropyl)trimethoxy silane, γ-(2-aminoethyl)aminopropyl trimethoxy silane, γ-chloropropyl trimethoxy silane, γ-mercaptopropyl trimethoxy silane, and γ-aminopropyl triethoxy silane; and an organic metal compound such as an organic titanium compound, an organic aluminium compound and

an organic zirconium compound. The silane coupling agent or organic metal compound may be used in the form of a 0.1-5% solution in an organic solvent such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, methyl alcohol, ethyl alcohol, propyl alcohol and butyl alcohol. Subsequently, the surface treatment solution may be applied uniformly over the substrate by means of, e.g., a spinner, followed by drying at 80 to 140°C for 10 to 60 min. to achieve the surface treatment.

[0073] After the application of the paste onto the substrate has been completed, the coating film is exposed with light using an exposure device. The exposure device which may be used is, for example, a proximity exposer. In the case where a large area is to be exposed, the paste is applied onto the substrate and then the exposure may be performed while conveying the paste-applied substrate, whereby the exposure of such a large area can be achieved even using an exposure device with a small light source.

[0074] After the exposure has been completed, development may be performed utilizing the difference in solubility in a developing solution between the exposed regions and the unexposed regions of the coating film. The development may be performed by, for example, a dipping method, spraying method or brushing method. As the developing solution, an organic solvent may be used into which the organic component in the paste can dissolve. Water may be added to the organic solvent in such an amount that the solubility of the organic component in the organic solvent is not impaired. It is preferred that the developing solution mainly consists of water. When a compound having an acidic group (e.g., a carboxyl group) is present in the paste, the development can be performed with an aqueous alkaline solution. As the aqueous alkaline solution, an aqueous solution of, for example, sodium hydroxide, sodium carbonate or calcium hydroxide may be used. However, it is preferred to use an aqueous solution of an organic alkaline compound for easy removal of alkaline components during the firing.

[0075] The organic alkaline compound may be a common amine compound. Specific examples of the amine compound include tetramethylammonium hydroxide, trimethylbenzylammonium hydroxide, monoethanol amine and diethanol amine.

[0076] The concentration of the alkaline solution is generally in the range of from 0.05 to 5 wt%, more preferably 0.1 to 1 wt%. If the alkali concentration is too low, then the soluble portions may not be removed. If the alkali concentration is too high, then peeling of patterned portions and corrosion of soluble portions may occur. The temperature for development is preferably 20 to 50°C, from a process control viewpoint.

[0077] Subsequently, firing may be performed in a firing furnace. The atmosphere and temperature for firing may depend on the types of the paste and substrate used. Firing is generally performed in an atmosphere of, for example, air, nitrogen or hydrogen. The firing furnace which may be used is a batch-type firing furnace or a belt-type continuous firing furnace.

[0078] The firing is generally performed at a temperature of 400 to 1,000°C. In the case where a pattern is formed on a glass substrate, it is preferable to maintain the temperature for firing at 480 to 610°C for 10 to 60 min. to ensure the firing.

[0079] According to the process embodiment as mentioned above, a display member can be produced which has a pattern consisting substantially of inorganic materials formed on a substrate.

[0080] Hereinbelow, embodiments of the present invention will now be described in more detail with reference to the following Examples. Unless otherwise stated, concentrations (%) are expressed as wt% (percent by weight).

[Examples 1 to 10, Comparative Examples 1 and 2]

[0081] A urethane and a polymer solution shown in Table 1, a dispersing agent (3 wt%), a levelling agent (3 wt%) and dipropylene glycol monomethyl ether (4 wt%) were dissolved in each other while heating to 50°C to prepare an organic solution. The organic solution was applied onto a glass substrate and then dried at 100°C for 90 min to form a coating film having a thickness of 30 μm . The haze of the coating film was measured using a direct-reading haze computer HGM-2DP (a product of Suga Test Instruments Co. Ltd.). The measured value for each sample is shown in Table 2.

[0082] To the organic solution was added inorganic fine particles shown in Table 1. The resulting mixture was kneaded using a kneader to prepare a paste.

[0083] The paste was heated to 500°C and 1,000°C at a rate of 10°C/min. Each of the weights at these temperatures was determined in an air atmosphere using a thermogravimetric analyzer "TGA-50" (a product of Shimadzu Corporation). The determined value of (weight at 500°C)/(weight at 1,000°C) for each sample is shown in Table 2.

[0084] Subsequently, the paste was applied onto a silicon wafer (diameter: 100 ± 0.5 mm, thickness: 525 ± 25 μm ; a product of Shin-Etsu Handotai Co., Ltd.) to form a coating film having a thickness of 3 to 10 μm . The coating film was heated to 30 to 500°C over 1 hour, and the stress of the coating film generated during this period was measured using a thin film stress meter "F2300S" (a product of FLEXUS). The maximum value among the measured stress values for each sample is shown in Table 2.

[0085] Separately, the paste was applied onto a glass substrate to form a coating film having a thickness of 50 μm .

The coating film was fired at 560°C for 15 min. After firing, the reflectance of the film which consisted substantially of inorganic materials was determined using an automatically recording spectrophotometer (a product of Hitachi Ltd.). The determined value for each sample is shown in Table 2.

[0086] Stripe-shaped address silver electrodes (line width: 100 μm , thickness: 3 μm , pitch: 500 μm) were formed on a glass substrate (diagonal size: 42 inches), and a dielectric layer was then formed thereon. The paste was used to perform the screen printing of a lower layer. A screen printing plate for the formation of a grid-shaped barrier rib pattern for a plasma display (each transversal barrier rib: line width 500 μm , pattern pitch 1,000 μm ; each longitudinal barrier rib: line width 60 μm , pattern pitch 500 μm) was arranged so that every transversal barrier rib and every address electrode crossed each other at right angles. The printing and drying of the paste were repeated 5 to 6 times while taking alignment until the dry thickness of the upper layer became 90 μm .

[0087] The paste was used to perform screen printing of a stripe pattern of an upper layer on the grid-shaped barrier rib pattern of the lower layer. A screen printing plate (each transversal barrier rib: line width 60 μm , pattern pitch 500 μm) was arranged so that every stripe line and every address electrode became parallel to each other. The printing and drying of the paste were repeated 5 to 6 times while taking alignment until the dry thickness of the upper layer reached 90 μm .

[0088] The grid-shaped barrier rib pattern formed as above was further fired at 560°C for 15 min. to produce a display member having grid-shaped barrier ribs formed by the stripe-shaped barrier ribs (pitch: 500 μm , line width: 60 μm , height: 130 μm) and the auxiliary barrier ribs (pitch: 1,000 μm , line width: 500 μm , height: 60 μm) crossing over the stripe-shaped barrier ribs at right angles. After firing, the presence of defects including peeling and line breaking was observed. The results are shown in Table 2.

[0089] Subsequently, a phosphor was applied between the adjacent barrier ribs in the display member. The application of the phosphor was performed by a dispenser method, in which a paste of the phosphor was discharged from the tip of a nozzle where a hole having a bore size of 130 μm was formed. The phosphor was applied on the side walls of the barrier ribs at a post-firing thickness of 25 μm and on the dielectric layer at a post-firing thickness of 25 μm and then fired at 500°C for 10 min. to produce a rear substrate. The rear substrate and a front substrate which had been produced separately, were stacked together with a sealing glass, and then neon gas containing 5% of xenon was introduced between them so that the internal gas pressure became 66,500 Pa. A driving circuit was then connected to produce a PDP.

[0090] To evaluate the reliability of the PDP, the PDP was left to stand for 2 months without turning on and then subjected to an acceleration test at 70°C for 48 hours. The increased voltage of the operating voltage was determined. The results are shown in Table 2. In the results, the increased voltage was classified into three levels as follows:

- stable: the voltage was increased by 1 V or less;
- slightly increased: the voltage was increased by 2 to 3 V; and
- increased: the voltage was increased by 4 V or more.

Table 1

	Urethane				Polymer solution		Low melting glass	Filler	Oxide fine particles
	Type	Amount (%)	Weight mean M.W.	EO content	Type	Amount (%)	Amount (%)	Amount (%)	Amount (%)
Ex. 1	I	10	18000	30%	I	20	60	-	-
Ex. 2	II	10	19000	10%	II	20	40	20	-
Ex. 3	III	10	42000	0%	I	20	60	-	-
Ex. 4	IV	10	27000	7%	II	20	40	17	3
Ex. 5	V	10	24000	80%	I	20	60	-	-
Ex. 6	VI	10	1200	50%	II	20	60	-	-
Ex. 7	I	0.05	18000	30%	I	20	60	-	-
Ex. 8	II	25	19000	10%	II	20	50	5	5
Ex. 9	I	10	18000	30%	I	50	30	-	-
Ex. 10	-	-	-	-	I	45	40	5	-
C.Ex. 1	-	-	-	-	I	30	60	-	-
C.Ex. 2	-	-	-	-	II	50	30	10	-

Table 2

	Haze of organic component-applied film (%)	Weight ratio (500°C/1000°C)	Maximum stress (MPa)	Reflectance (%)	Defect(s)	Operating voltage
Ex. 1	0.2	1.01	6	20	0	Stable
Ex. 2	0.3	1.00	5	43	0	Stable
Ex. 3	70.0	1.00	4	20	4	Stable
Ex. 4	15.0	1.01	3	61	0	Stable
Ex. 5	0.1	1.03	13	20	4	Slightly increased
Ex. 6	0.0	1.01	15	20	5	Stable
Ex. 7	0.1	1.03	17	20	5	Slightly increased
Ex. 8	0.1	1.00	4	79	3	Stable
Ex. 9	0.2	1.04	11	20	4	Slightly increased
Ex. 10	0.0	1.04	16	38	5	Slightly increased
C.Ex. 1	0.0	1.08	24	20	>50	Increased
C.Ex. 2	0.0	1.10	25	48	>50	Increased

[Examples 11 to 21, Comparative Examples 3 and 4]

[0091] A urethane, an amine compound, a monomer and a polymer solution shown in Table 3, a photopolymerization initiator (5 wt%), an organic dye (0.01 wt%) and γ -butyrolactone (5 wt%) were dissolved while heating the mixture to 50°C to prepare an organic solution. Inorganic fine particles shown in Table 3 were added to the organic solution. The mixture was kneaded using a kneader to prepare a paste.

[0092] The haze of a film on which the organic component was applied (i.e., an organic component-applied film), the weights of the paste at 500°C and 1,000°C, the stress of a paste coating film and the post-firing reflectance of the paste coating film were determined in the same manner as in Example 1. The determined values are shown in Table 4.

[0093] Stripe-shaped address silver electrodes (line width: 50 μm , thickness: 3 μm , pitch: 250 μm) were formed on a glass substrate (diagonal size: 42 inches), and then a dielectric layer having a thickness of 15 μm was formed thereon. The paste was applied over the dielectric layer and then dried so that the dry thickness of the paste became 90 μm .

[0094] A photomask for the formation of barrier ribs for a plasma display (stripe-shaped pattern, line width: 600 μm , pattern pitch: 1000 μm) was arranged so that every pattern line and every address electrode crossed each other at right angles, and then exposed to light. In this process, a gap of 100 μm was provided between the photomask and the surface of the coating film in order to prevent contamination of the photomask. A lowest value among the exposure levels at which no peeling of the barrier rib pattern was observed during development was taken as the minimum exposure level.

[0095] After exposure, the paste was further applied and dried to form a coating film having a dry thickness of 90 μm . A photomask (stripe-shaped pattern, line width: 30 μm , pattern pitch: 250 μm) was arranged on the coating film so that every pattern line and every address electrode became parallel to each other, and then exposed with light. After exposure, the resultant product was developed in a 0.5% aqueous ethanol amine solution and then fired at 560°C for 15 min. In this manner, a display member was produced which had grid-shaped barrier ribs formed by the stripe-shaped barrier ribs (pitch: 250 μm , line width: 30 μm , height: 130 μm) and the auxiliary barrier ribs (pitch: 1,000 μm , line width: 600 μm , height: 60 μm). After firing, the presence of defects including peeling and line breaking was observed. The results are shown in Table 4.

[0096] Subsequently, a phosphor was applied between the adjacent barrier ribs. The application of the phosphor was performed by a dispenser method, in which a paste of the phosphor was discharged from the tip of a nozzle where a hole having a bore size of 130 μm was formed. The phosphor was applied on the side walls of the barrier ribs at a post-firing thickness of 25 μm and on the dielectric layer at a post-firing thickness of 25 μm , and then fired at 500°C for 10 min, thereby producing a rear substrate for a PDP. The rear substrate and a front substrate, which had been produced separately, were stacked together with a sealing glass, and then neon gas containing 5% of xenon was introduced between them so that the internal gas pressure became 66,500 Pa. A driving circuit was then connected to produce a PDP.

[0097] To evaluate the reliability of the PDP, the PDP was left to stand for 2 months without turning on and then subjected to an acceleration test at 70°C for 48 hours. The increased voltage of the operating voltage was determined. The results are shown in Table 4. In the results, the increased voltage was classified into three levels as follows:

stable: the voltage was increased by 1 V or less;

slightly increased: the voltage was increased by 2 to 3 V; and

increased: the voltage was increased by 4 V or more.

Table 3

	Urethane				Amine compound		Monomer		Polymer solution		Low melting glass	Filler	Oxide fine particles Amount (%)	Concentration of ethylenic unsaturated bond
	Type	Amount (%)	Weight: mean M.W.	EO content	Type	Amount (%)	Type	Amount (%)	Type	Amount (%)				
Ex. 11	VII	4	18000	30%	I	3	I	3	III	30	50	0	0	0.45
Ex. 12	VIII	4	19000	10%	II	6	-	0	IV	30	40	10	0	0.83
Ex. 13	VII	4	18000	30%	-	0	I	6	III	30	50	0	0	0.36
Ex. 14	VIII	0.05	19000	10%	II	5	II	4.95	III	30	40	7	3	0.83
Ex. 15	VII	25	18000	30%	-	0	-	0	IV	15	50	0	0	0.25
Ex. 16	III	4	42000	0%	I	3	II	3	V	50	30	0	0	0.27
Ex. 17	IV	4	27000	7%	II	3	I	3	III	45	40	5	0	0.66
Ex. 18	V	4	24000	80%	I	3	I	3	IV	45	40	5	0	0.61
Ex. 19	VI	4	1200	50%	II	3	II	3	V	30	40	5	5	0.39
Ex. 20	-	0	-	-	II	3	II	7	III	30	50	0	0	0.69
Ex. 21	-	0	-	-	I	3	I	7	IV	30	40	10	0	0.61
C.Ex. 3	-	0	-	-	II	10	-	0	III	30	60	0	0	1.19
C.Ex. 4	-	0	-	-	I	0	I	5	V	45	30	10	0	0.15

Table 4

	Haze of organic component-applied film (%)	Weight ratio (500°C/1000°C)	Maximum stress (MPa)	Reflectance (%)	Minimum exposure level (mJ/cm ²)	Defect (s)	Operating voltage
Ex. 11	0.2	1.02	6	20	500	0	Stable
Ex. 12	0.3	1.02	4	43	300	0	Stable
Ex. 13	0.2	1.02	5	20	1100	0	Stable
Ex. 14	0.3	1.03	13	61	300	0	Slightly increased
Ex. 15	0.1	1.01	5	20	500	4	Stable
Ex. 16	72.0	1.00	3	20	500	4	Stable
Ex. 17	15.0	1.02	6	38	400	5	Stable
Ex. 18	0.0	1.04	14	40	400	5	Slightly increased
Ex. 19	0.0	1.01	13	79	500	4	Stable
Ex. 20	0.0	1.05	17	20	300	7	Slightly increased
Ex. 21	0.0	1.04	16	45	400	8	Slightly increased
C.Ex. 3	0.0	1.08	24	20	150	>50	Increased
C.Ex. 4	0.0	1.10	25	53	1500	>50	Increased

[Examples 22 to 24, Comparative Example 5]

[0098] A urethane, an amine compound, a monomer and a polymer solution shown in Table 5, and a photopolymerization initiator (2 wt%) and an organic dye (0.01 wt%) were dissolved in each other while heating to 50°C to prepare an organic solution. To the organic solution were added fine silver particles (mean particle size: 1.5 μm , specific surface: 1.10 m^2/g) (70 wt%) and fine bismuth borosilicate glass particles (3 wt%). The resultant mixture was kneaded with a kneader to prepare a paste.

[0099] The haze of a film on which the organic component was applied (i.e., an organic component-applied film), the weights of the paste at 500°C and 1,000°C and the stress of a paste coating film were determined in the same manner as in Example 1. The determined values for each sample are shown in Table 6.

[0100] The paste containing the fine silver particles prepared above was applied onto a glass substrate (diagonal size: 42 inches) by a screen printing method to form a coating film having a thickness of 6 μm . The coating film was then exposed with light through a photomask (stripe-shaped pattern, pattern pitch: 250 μm , line width: 100 μm), and then developed in a 0.5% aqueous ethanol amine solution to form a stripe-shaped electrode pattern. The glass substrate having the processed electrode pattern was dried at 80°C for 15 min. and then fired at 580°C for 15 min. to form an electrode. In the electrode pattern after the firing, the presence of defects including peeling and line breaking was observed. The results are shown in Table 6.

[0101] An dielectric layer was formed on the glass substrate with the electrode. A barrier rib pattern was then formed on the dielectric layer in the same manner as in Example 11.

[0102] Subsequently, a phosphor was applied between the adjacent barrier ribs of the display member. The application of the phosphor was performed by a dispenser method, in which a paste of the phosphor was discharged from the tip of a nozzle where a hole having a bore size of 130 μm was formed. The phosphor was applied on the side walls of the barrier ribs at a post-firing thickness of 25 μm and on the dielectric layer at a post-firing thickness of 25 μm , and then fired at 500°C for 10 min, thereby producing a rear substrate for a PDP. The rear substrate and a front substrate, which had been produced separately, were stacked together with a sealing glass, and then neon gas containing 5% of xenon was introduced between them so that the internal gas pressure became 66,500 Pa. A driving circuit was then connected to produce a PDP.

Table 5

	Urethane				Amine compound		Monomer		Polymer solution		Concentration of ethylenic unsaturated bond
	Type	Amount (%)	Weight mean M.W.	EO content	Type	Amount (%)	Type	Amount (%)	Type	Amount (%)	
Ex. 22	VII	4	18000	30%	I	3	III	3	III	15	0.36
Ex. 23	VIII	5	19000	10%	II	2	-	3	IV	15	0.41
Ex. 24	VII	7	18000	30%	-	0	III	3	III	15	0.18
C.Ex. 5	-	0	-	-	II	9	-	1	IV	15	1.05

Table 6

	Haze of organic component-applied film (%)	Weight ratio (500°C/1000°C)	Maximum stress (MPa)	Minimum exposure level (mJ/cm ²)	Defect (s)
Ex. 22	0.2	1.02	6	400	0
Ex. 23	0.3	1.02	7	450	0
Ex. 24	0.2	1.02	4	1100	0
C.Ex. 5	0.3	1.11	23	300	>10

Polymer solution I: ethyl cellulose (a 20 wt% solution in terpineol).

Polymer solution II: polymethyl methacrylate (a 50 wt% solution in toluene).

5 Polymer III: a polymer consisting of styrene/methyl methacrylate/methacrylic acid copolymer (weight composition ratio: 30/30/40) to which 40 parts by weight of glycidyl acrylate was added based on 100 parts by weight of the copolymer.

10 Polymer solution IV: a polymer consisting of methyl methacrylate/methacrylic acid copolymer (weight composition ratio: 60/40) to which 40 parts by weight of glycidyl acrylate was added based on 100 parts by weight of the copolymer (acid value of the resin: 115 mg KOH/g).

15 Polymer solution V: a polymer consisting of methyl methacrylate/methacrylic acid copolymer (weight composition ratio: 82/18) (acid value of the resin: 90 mg KOH/g).

Monomer I: dipentaerythritol hexaacrylate.

Monomer II: $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}-(\text{OCH}(\text{CH}_3)\text{CH}_2)_9-\text{OCOC}(\text{CH}_3)=\text{CH}_2$.

20 Monomer III: Propoxylated trimethylolpropane triacrylate.

Amine I: N,N-diethylaminoethyl methacrylate.

25 Amine II: bis(2-hydroxy-3-methacryloyloxypropyl) n-propylamine.

Urethane I: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a hydrogen atom; R^3 is an ethylene oxide-propylene oxide co-oligomer residue; and R^4 is an isophorone diisocyanate residue, and which has an ethylene oxide content of 30% and an entire molecular weight of 18,000.

30 Urethane II: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a hydrogen atom; R^3 is ethylene oxide-propylene oxide co-oligomer; and R^4 is an isophorone diisocyanate residue, and which has an ethylene oxide content of 10% and an entire molecular weight of 19,000.

35 Urethane III: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a hydrogen atom; R^3 is a butylene oxide oligomer residue; and R^4 is an isophorone diisocyanate residue, and which has an ethylene oxide content of 0% and an entire molecular weight of 42,000.

40 Urethane IV: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a hydrogen atom; R^3 is an ethylene oxide-butylene oxide co-oligomer residue; and R^4 is an isophorone diisocyanate residue, and which has an ethylene oxide content of 7% and an entire molecular weight of 27,000.

45 Urethane V: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a hydrogen atom; R^3 is an ethylene oxide-propylene oxide co-oligomer residue; and R^4 is an isophorone diisocyanate residue, and which has an ethylene oxide content of 80% and an entire molecular weight of 24,000.

Urethane VI: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a hydrogen atom; R^3 is an ethylene oxide-propylene oxide co-oligomer residue; and R^4 is a 1,4-cyclohexylene diisocyanate residue, and which has an ethylene oxide content of 50% and an entire molecular weight of 1,200.

50 Urethane VII: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is a methacrylic group; R^3 is an ethylene oxide-propylene oxide co-oligomer residue; and R^4 is an isophorone diisocyanate residue, and which has an ethylene oxide content of 30% and an entire molecular weight of 18,000.

55 Urethane VIII: a urethane compound which is represented by formula (1), wherein each of R^1 and R^2 is an acrylic group; R^3 is an ethylene oxide-propylene oxide co-oligomer residue; and R^4 is a 1,4-cyclohexylene diisocyanate residue, and which has an ethylene oxide content of 10% and an entire molecular weight of 19,000.

Low melting glass powder: composition (content of oxides): LiO_2 : 9%, SiO_2 : 22%, Al_2O_3 : 23%, B_2O_3 : 33%, BaO:

4%, ZnO: 2% and MgO: 7% (glass transition temperature: 472°C, softening point under load: 515°C, refractive index: 1.59, mean particle size: 2.55 µm).

Filler: composition (content of oxides): SiO₂: 38%, B₂O₃: 10%, BaO: 5%, Al₂O₃: 36%, ZnO: 2%, MgO: 5% and CaO₂: 4% (glass transition temperature: 652°C, softening point under load: 746°C, refractive index: 1.59, mean particle size: 2.4 µm).

Fine oxide particles: fine oxide particles (mean particle size: 0.005 µm)

[0103] A paste embodying the present invention can be used to provide a display member having a post-firing pattern with no defects.

Claims

1. A paste comprising a urethane compound and inorganic particles.
2. A paste according to Claim 1, wherein the content of the inorganic particles in the paste is in the range of from 40 to 80 wt%.
3. A paste according to Claim 1 or 2, wherein the urethane compound comprises a urethane compound having an ethylenic unsaturated group.
4. A paste according to any preceding Claim, wherein the urethane compound has a molecular weight ranging from 15,000 to 50,000.
5. A paste according to any preceding Claim, wherein the content of the urethane compound in the paste is in the range of from 0.1 to 20 wt%.
6. A paste according to any preceding Claim, wherein the urethane compound contains an ethylene oxide unit.
7. A paste according to Claim 1, wherein the urethane compound is represented by formula (1):



wherein R¹ and R² are independently selected from a substituent having an ethylenic unsaturated group, a hydrogen atom, a C₁-C₂₀ alkyl group, a C₁-C₂₀ aryl group, a C₁-C₂₀ aralkyl group and a C₁-C₂₀ hydroxyaralkyl group; R³ is an alkylene oxide group or an alkylene oxide oligomer; R⁴ is an organic group having a urethane bond; and n is an integer of from 1 to 10.

8. A paste according to Claim 7, wherein R³ is an oligomer containing an ethylene oxide unit and a propylene oxide unit and the content of the ethylene oxide unit in the oligomer is in the range of from 8 to 70 wt%.
9. A paste according to any preceding Claim, which further comprises an amine compound having an ethylenic unsaturated group.
10. A paste according to Claim 9, wherein the amine compound is represented by formula (3) or (4):



wherein R⁵ is a substituent having an ethylenic unsaturated group; R⁶, R⁷ and R⁸ are independently selected from a substituent having an ethylenic unsaturated group, a hydrogen atom, a C₁-C₂₀ alkyl group, a C₁-C₂₀ aryl group,

a C₁-C₂₀ aralkyl group and a C₁-C₂₀ hydroxyalkyl group; and M is a bivalent linking group.

11. A paste according to any preceding Claim, which further comprises a polymer having a carboxyl group.

12. A paste according to Claim 11, wherein the polymer having a carboxyl group has an ethylenic unsaturated group.

13. A paste according to any preceding Claim, wherein the inorganic particles comprise glass powder having a softening point under load of from 450 to 600°C.

14. A paste according to any preceding Claim, wherein the inorganic particles contain 60 to 97 wt% of glass powder having a softening point under load up to 600°C and 3 to 40 wt% of a filler having a mean particle size of from 1 to 4 µm.

15. A paste according to Claim 14, wherein the inorganic particles further contain not more than 30 wt% of fine oxide particles having a mean particle size of from 0.003 to 0.02 µm.

16. A paste according to any preceding Claim, which paste, when heated to 500°C and 1,000°C, has respective weights at these temperatures which satisfy the following equation:

$$(\text{weight at } 500^{\circ}\text{C}) / (\text{weight at } 1,000^{\circ}\text{C}) \leq 1.05.$$

17. A paste according to any preceding Claim, which paste, when applied onto a silicon wafer into a thin film and then heated to 500°C, has a calculated maximum value of the average film stress, based on the quantity of warping of the silicon wafer caused by shrinkage of the thin film, in the range of from 0.1 to 20 MPa.

18. A paste according to any preceding Claim, wherein the paste is photosensitive.

19. A paste according to Claim 18, at least one component of which has one ethylenic unsaturated bond therein and wherein the concentration of ethylenic unsaturated bonds in the paste, prior to irradiation with an active light, is in the range of from 0.2 to 1.0 mol per kg of the paste.

20. Use of a paste according to any preceding Claim, in production of a display.

21. Use according to Claim 20, wherein the display is a plasma display.

22. A paste comprising inorganic particles and an organic component, which paste, when heated to 500°C and 1,000°C, has respective weights at these temperatures satisfying the following equation:

$$(\text{weight at } 500^{\circ}\text{C}) / (\text{weight at } 1,000^{\circ}\text{C}) \leq 1.05.$$

23. A paste comprising inorganic particles and an organic component, which paste, when applied onto a silicon wafer to form a thin film and then heated to 500°C, has a calculated maximum value of the average film stress, based on the quantity of warping of the silicon wafer caused by shrinkage of the thin film, in the range of from 0.1 to 20 MPa.

24. A process for producing a display member, comprising applying a paste comprising a urethane compound and inorganic particles onto a substrate and then firing the applied paste.

25. A process according to Claim 24, wherein the content of the inorganic particles in the paste is in the range of from 40 to 80 wt%.

26. A process according to Claim 24 or 25, wherein the urethane compound has an ethylenic unsaturated group.

27. A process according to Claim 24, 25 or 26, wherein the urethane compound has a molecular weight ranging from 15,000 to 50,000.

28. A process according to any one of Claims 24 to 27, wherein the content of the urethane compound in the paste is

in the range of from 0.1 to 20 wt%.

29. A process according to any one of Claims 24 to 28, wherein the urethane compound contains an ethylene oxide unit.

30. A process according to any one of Claims 24 to 29, wherein the urethane compound is represented by formula (1) :

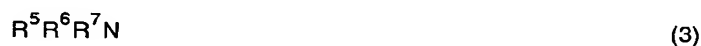


wherein R^1 and R^2 are independently selected from a substituent having an ethylenic unsaturated group, a hydrogen atom, a C_1 - C_{20} alkyl group, a C_1 - C_{20} aryl group, a C_1 - C_{20} aralkyl group and a C_1 - C_{20} hydroxyaralkyl group; R^3 is an alkylene oxide group or an alkylene oxide oligomer; R^4 is an organic group having a urethane bond; and n is an integer of from 1 to 10.

31. A process according to Claim 30, wherein R^3 is an oligomer containing an ethylene oxide unit and a propylene oxide unit and the content of the ethylene oxide unit in the oligomer is in the range of from 8 to 70 wt%.

32. A process according to any one of Claims 24 to 31, wherein the paste further comprises an amine compound having an ethylenic unsaturated group.

33. A process according to Claim 32, wherein the amine compound is represented by formula (3) or (4):



wherein R^5 is a substituent having an ethylenic unsaturated group; R^6 , R^7 and R^8 are independently selected from a substituent having an ethylenic unsaturated group, a hydrogen atom, a C_1 - C_{20} alkyl group, a C_1 - C_{20} aryl group, a C_1 - C_{20} aralkyl group and a C_1 - C_{20} hydroxyalkyl group; and M is a bivalent linking group.

34. A process according to any one of Claims 24 to 33, wherein the paste further comprises a polymer having a carboxyl group.

35. A process according to Claim 34, wherein the polymer having a carboxyl group has an ethylenic unsaturated group.

36. A process according to any one of Claims 24 to 35, wherein the inorganic particles comprise glass powder having a softening point under load of from 450 to 600°C.

37. A process according to any one of Claims 24 to 36, wherein the inorganic particles contain 60 to 97 wt% of glass powder having a point under load up to 600°C and 3 to 40 wt% of a filler having a mean particle size of from 1 to 4 μ m.

38. A process according to Claim 37, wherein the inorganic particles contain not more than 30 wt% of fine oxide particles having a mean particle size of from 0.003 to 0.02 μ m.

39. A process according to any one of Claims 24 to 38, which paste, when heated to 500°C and 1,000°C, has respective weights at these temperatures which satisfy the following equation:

$$(\text{weight at } 500^\circ\text{C}) / (\text{weight at } 1,000^\circ\text{C}) \leq 1.05.$$

40. A process according to any one of Claims 24 to 39, which paste, when applied on a silicon wafer to form a thin film and then heated to 500°C, has a calculated maximum value of the average film stress, based on the quantity of warping of the silicon wafer caused by shrinkage of the thin film, from 0.1 to 20 MPa.

41. A process according to any one of Claims 24 to 40, wherein the paste is photosensitive.

42. A process according to Claim 41, which process comprises applying the paste, patterning the paste by photolithography method and then firing the patterned paste.

5 43. A process according to any one of Claims 24 to 42, wherein the paste comprises at least one component which has an ethylenic unsaturated bond therein and the concentration of the ethylenic unsaturated bond in the paste, prior to irradiation with an active light, is in the range of from 0.2 to 1.0 mol per kg of the paste.

44. A process according to any one of Claims 24 to 43, wherein the display is a plasma display.

10 45. A display member comprising a substrate having thereon a fired layer of a paste composition comprising a urethane compound and inorganic particles.

46. A display having a display member according to Claim 45.

15 47. A display according to Claim 46, which is a plasma display.

48. A process for producing a display member, comprising applying a paste according to Claim 22 or 23 onto a substrate and then firing the paste.

20 49. A process according to Claim 48, wherein the display is a plasma display.

50. A display member comprising a substrate having thereon a fired layer of a paste composition selected from (a) a composition which when heated to 500°C and 1,000°C, has respective weights at these temperatures satisfying the following equation:

$$(\text{weight at } 500^{\circ}\text{C}) / (\text{weight at } 1,000^{\circ}\text{C}) \leq 1.05$$

30 and (b) a composition which when applied onto a silicon wafer to form a thin film and then heated to 500°C, has a calculated maximum value of the average film stress, based on the quantity of warping of the silicon wafer caused by shrinkage of the thin film, in the range of from 0.1 to 20 MPa.

51. A display having a display member according to Claim 50.

35 52. A display according to Claim 51, which is a plasma display.

(19)



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(54) **Paste, display member, and process for production of display member**

(57) A display member, particularly a plasma display member, can be produced by a process comprising applying a paste which comprises a urethane compound and inorganic particles onto a substrate and then firing

the paste, so providing a display member having a post-firing pattern without any defect.

EP 1 158 019 A3



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